

DISULFOTON GROUND-WATER MONITORING

SUBJECT: Additional Clarification of Disulfoton Ground-Water Monitoring Data Assessment

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DATE: February 7, 2000 (modification of January 6, 2000 memo. The earlier memo reported the detections in the USGS NAWQA program incorrectly as ground-water samples rather than surface-water samples. The modified memo correctly cites the detections as surface-water detections. This memo replaces the memo dated January 6, 2000).

Background: A Water Assessment for Disulfoton, which included modeling and monitoring data, was completed December 11, 1997 (out of EFED on 12/15/97) and modified for the RED (10/07/98). SRRD had questions concerning the disulfoton detections in ground water in studies conducted by Virginia Polytechnic Institute and State University (VPI&SU, Mosaghimi, 1989) in Virginia where disulfoton concentrations ranged from 0.04 to 2.87 µg/L and in a Wisconsin Department of Natural Resources study in Wisconsin (WDNR, after Barton, 1982) where concentrations ranged from 4.00 to 100.00 µg/L. Of specific interest is that the concentrations of parent disulfoton reported in these studies (VA and WI) exceeded the estimate of 0.05 µg/L obtained from EFED's SCI-GROW (ground-water screening model) model. The SCI-GROW estimated concentration of total disulfoton was 3.19 µg/L, although no monitoring data are available for comparison. The SCI-GROW model represents a "vulnerable site", but not necessarily the most vulnerable, treated (here) with the maximum rate and number of disulfoton applications, while assuming conservative environmental properties (90 percent upper confidence bound on the mean aerobic soil half-life and an average K_{oc} value). The degradates were assumed to have the same mobility as parent disulfoton and the 90 percent upper bound on the mean half-life of the total residues was used for the total disulfoton residues. The USGS NAWQA program has not detected disulfoton in ground water with a detection limit of 0.017 µg/L.

Only summary information for these two monitoring studies was available during the initial water assessment development. Additional information for these studies was located and is presented in this document. Even with this additional information, our knowledge of these studies is still very sketchy. I have attempted to reevaluate the information and better clarify our understanding. This memo primarily addresses the parent disulfoton and considers the additional information that was not previously available. I will summarize disulfoton metabolites (D. sulfone and D. sulfoxide) for clarity, but there is no additional information concerning the metabolites. Further, this memorandum is primarily concerned with disulfoton residues found in ground water. Although, I have included a summary of the parent disulfoton concentrations observed in surface water in the Virginia study.

Summary and Recommendations: The several points were considered (in addition to the noted QA/QC problems) while making these recommendations. First, the Virginia and Wisconsin monitoring studies were probably conducted in areas vulnerable to ground-water contamination. The level of certainty with respect to vulnerability is probably greater for Wisconsin (relatively less uncertainty) than for Virginia (relatively more uncertainty). The occurrence of preferential flow and transport processes has been noted in Wisconsin (and is also possible in Virginia) and may (speculation) have contributed to the "high" concentrations (especially in WI) when the initial sampling occurred, but not necessarily in the follow-up sampling. The knowledge concerning the disulfoton use in areas in association with the wells is not well known (high uncertainty).

A second point is the ground-water monitoring data in the STORET data base. The STORET data base compiles results from ground-water and surface-water monitoring conducted by government, non-government, and academic sources. Thus, these studies have a wide degree of variability because of differences in such factors as study goals, study designs, site selection criteria, and detection limits. Frequently, STORET merely reports disulfoton concentrations as being less than a value (e.g., typically the detection limit which ranged from $< 1 \mu\text{g/L}$ up to $250 \mu\text{g/L}$), so there is high degree of uncertainty of concentrations because of variable, but often high limits of detections.

Excluding the $2.87 \mu\text{g/L}$ value reported for VA, the other detections in VA corresponded reasonably well with the detection limit of the NAWQA study ($0.017 \mu\text{g/L}$). The monitoring sites and detections in these data bases, especially NAWQA study areas do not necessarily target "highly vulnerable" areas such as the Central Sand Plains in Wisconsin. Disulfoton parent is not very persistent in aerobic soil conditions which may explain the lack of detections in follow-up monitoring in Wisconsin. There is no information presented by Mostaghimi et al. to suggest that the USEPA should not consider the disulfoton detections reported in the Virginia study.

The issue of the QA/QC on the monitoring data collected by the Wisconsin Department of Natural Resources (WDMR. after Barton, 1982) and failure of follow-up sampling to detect disulfoton residues in ground water as suggested by Holden (1986) has been considered by EFED in the ground-water quality assessment. The Central Sands of Wisconsin are known to be highly vulnerable to ground-water contamination. There are regions within the United States that have

conditions that are highly vulnerable to ground-water contamination and regularly have pesticides detected in ground water which far exceeds values seen elsewhere. Several of these areas are well documented, e.g., Long Island, Suffolk County, NY and Central Sand Plain in WI. Although, some questions have been levied against the disulfoton detections in Wisconsin, the occurrence of disulfoton at the levels reported can not be ruled out.

Recommendations: It is recommended that the Virginia data be considered in the "quantitative" drinking water assessment for ground water. The Wisconsin data should be noted and addressed more qualitatively. Highly vulnerable areas, such as the Central Sand Plain, do not represent the entire use area and can probably be better mitigated or managed at a local or state level. Specifically, it is recommended that the 2.87 µg/L be used for chronic exposure from ground water and the SCI-GROW value of 3.19 µg/L be used for acute ground-water exposure. Based upon the fate properties of disulfoton, the sulfoxide and sulfone degradates (more persistent and probably more mobile) have a greater probability of being found in ground water. It is likely that a ground-water monitoring study (ies) may be required to better assess the potential exposure from the degradates (and also parent).

Monitoring Studies With Disulfoton Detections in Ground Water

Virginia: Mostaghimi, S. 1986-1990. Virginia Polytechnic Institute and State University

A monitoring study was conducted to evaluate the effectiveness of Best Management Practices (BMP) in a 3616 acre watershed in the Nomini Creek Watershed, Westmoreland County, Virginia. Approximately half of the watershed is in agriculture and the other half is forested. The major focus of this study was surface-water quality rather than ground-water quality. However, in addition to the surface-water monitoring, twelve wells were analyzed for pesticides, including disulfoton. Although this memorandum is primarily concerned with disulfoton residues in ground water, I will also briefly present the information on the levels of disulfoton reported in surface water during the Virginia study.

Ground Water: Samples were taken in 1985 and 1986 from four household wells in the Nomini Creek Watershed (NCW). Water samples from these wells were analyzed for 24 pesticides. Detectable levels of (not specified) pesticides were found in all four wells at concentrations below the respective MCL. One of these four household wells consistently had higher pesticide levels than the other wells. The study authors suggested that this household well was not "sufficiently protected and was contaminated by surface runoff from adjacent land".

Based upon these results of the four household wells sampled, eight pairs of ground-water monitoring wells (39 to 54 feet deep) were installed at eight sites in the NCW and sampled approximately monthly from June 1986 through December 1990. Information concerning farming practices in the watershed were obtained from farmer interviews and questionnaires. Disulfoton residues (0.04, 0.10, 0.10, 0.13, 0.16, and 2.87 µg/L) were detected in wells at five of the eight monitoring sites during the period 11/86 to 12/90. The average detection was 0.57 µg/L

(standard deviation = 1.13 µg/L). Since the study authors present no information or discussion questioning the pesticide detections which occurred in the monitoring wells (notably site GN3, the well with 2.87 µg/L), the disulfoton detections found in the monitoring wells should be included in this assessment.

Table 1. Summary of Disulfoton Detections in ground water from the eight ground-water monitoring wells in Nomini Creek Watershed (Virginia), during 1986 and 1987.

Sampling Date	Well-Site Number	Concentration (µg/L)
11/5/86	GN3	2.87
11/5/86	GN6	0.04
3/13/87	GN4	0.10
8/20/87	GN1	0.13
8/20/87	GN2	0.16
8/20/87	GN3	0.10

The study was conducted under a Quality Assurance/Quality Control Plan. Pesticides were determined using GLC methods with an EC Ni63 detector. The study reportedly ran until 1995 (data available only goes through 1990).

Surface Water: The detections of parent disulfoton in surface-water samples (0.037 to 6.11 µg/L) collected in the Nomini Creek Watershed study fell within an order of magnitude with the estimated environmental concentrations (EECs) obtained from the PRZM/EXAMS models for parent disulfoton which range from 0.21 to 1.14 µg/L for annual mean daily concentrations and 7.14 to 26.75 µg/L for peak daily values.

Table 2. Disulfoton detections in surface-water samples collected in the Nomini Creek Watershed (Virginia), during 1986.

Sample date	Site Number: Sample #	Concentration (µg/L)
8/18/86	QN1:1 (9:13 am)	6.11
8/18/86	QN1:2 (12:25 pm)	0.37
9/28/86	QN2: (only 1 sample)	1.62

Wisconsin: Barton, 1982. In May and June 1982, the Wisconsin Department of Natural Resources (WDNR) sent twenty-nine water samples from wells in the Central Sands area of Wisconsin to the EPA's Office of Pesticide Programs for pesticide residue analysis. Samples were taken from one municipal well, two or three community wells, and twenty-five home wells; all of which were sources of drinking water.

Of the 29 samples, 15 samples were reported as no detects whereas 14 samples were reported disulfoton detections. Disulfoton detections ranged from 4.00 to 100.00 µg/L, with a mean (samples with detections) of 38.43 µg/L and standard deviation of 31.56 µg/L. No detection limit was specified for disulfoton, although detections as low as 1 µg/L are reported for other pesticide residues (aldicarb, and aldicarb sulfone, dinoseb, sencor, linuron, carbofuran, and Lasso/Bravo).

Holden (1986) wrote that the WDNR sampling program was criticized for a number of reasons including that the quality assurance and quality control procedures (QA/QC) were not always followed during some stages of sampling and analysis (Holden, 1986). Holden (1986) further indicates that "Harkin et al. (1984) noted in their WIS WRC report *Pesticides in Groundwater beneath the Central Sand Plain of Wisconsin* that some detections of pesticides in initial screening were false positives and were not supported by resampling and reanalysis by more sensitive analytical methods."

Aldicarb and aldicarb sulfone were also found in this study and in follow up studies, while disulfoton was apparently not found in follow-up sampling. Aldicarb is no longer registered for use in Wisconsin.

The criticisms of the WDNR study must, however, be put in some sort of perspective. First, a study that did not follow QA/QC criteria does not and should not automatically mean that the data is bad or wrong, the detections may be correct (presence and magnitude). Frequently "older" monitoring studies often had problems associated with them, such as QA/QC problems, limited pesticide usage information, and no knowledge about the study area's hydrology. Frequently, studies with QA/QC programs are poorly designed, so that the results may be meaningless. I suspect that with further investigation more of these old studies with "no detections" have questionable results than those that have "positive" detections.

Pesticide residues not being found in follow-up sampling may be the result of dissipation processes and should not be used to discount detections in earlier samples. The environmental fate properties and site hydrology must also be considered. Because ground water is a dynamic system, pesticides may be present at one sampling event and not at another. So when the sample is collected, in relationship to pesticide use and rainfall, is important. All that can be said is that residues were not found in follow-up samples. It is unknown which samples were re-analyzed with more sensitive methods.

The disulfoton detections in the Central Sand Plain may have been the result of preferential flow and transport processes. Literature documents preferential flow in the Central Sand Plain. Thus,

disulfoton residues may have by-passed the soil matrix and gone directly to ground water which is possibly reflected in the "high" level of the detections. Although preferential flow is currently an ongoing area of research and much remains unknown, it is known that preferential flow is influenced by a number of factors, including rainfall amounts, intensity, and frequency.

Disulfoton generally appears to be not very persistent under aerobic soil conditions and therefore may also not be very persistent in aquifers that are aerobic. Therefore it may have also been missed by utilizing a predetermined sampling schedule (e.g., monthly). Whereas a persistent chemical, such as aldicarb and aldicarb sulfone, will be found at greater frequencies and be less dependent upon timing of sampling. Disulfoton usage history before the detections and prior to the follow-up sampling is not specified.

USGS Surface-Water Monitoring for Disulfoton

The USGS National Water-Quality Assessment Program (NAWQA) study reports parent disulfoton concentrations in surface water ranging <0.017 to 0.060 µg/L, with the 99.5th and 99.9th percent concentration were 0.020 and 0.060 µg/L, respectively. The analytical limit of detection is 0.017 µg/L (USGS, 1998). There is considerable uncertainty about the vulnerability of the sampling sites and the disulfoton usage patterns in areas around the sampling sites (e.g., monitoring is not necessarily designed to specifically look for disulfoton).

CITATIONS

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